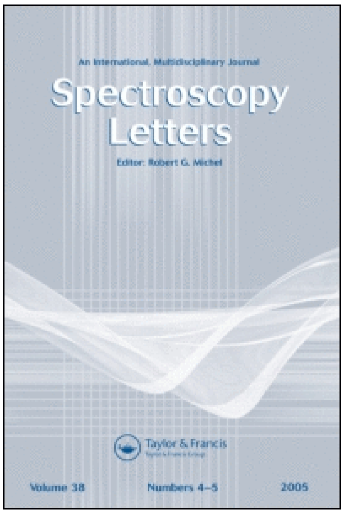

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Hydrolysis of Titanium Tetrabutoxide. Study by FT-IR Spectroscopy

M. J. Velasco[a]; F. Rubio[a]; J. Rubio[a]; J. L. Oteo[a]
[a] Instituto de Cerámica y Vidrio (C.S.I.C.)., Madrid, Spain

To cite this Article Velasco, M. J. , Rubio, F. , Rubio, J. and Oteo, J. L.(1999) 'Hydrolysis of Titanium Tetrabutoxide. Study by FT-IR Spectroscopy', Spectroscopy Letters, 32: 2, 289 — 304
To link to this Article: DOI: 10.1080/00387019909349984
URL: http://dx.doi.org/10.1080/00387019909349984

SPECTROSCOPY LETTERS, 32(2), 289-304 (1999)

HYDROLYSIS OF TITANIUM TETRABUTOXIDE. STUDY BY FT-IR SPECTROSCOPY.

Key words: Titanium alkoxide, hydrolysis, FT-IR, Deconvolution, Time Evolution.

Velasco M. J., Rubio F.*, Rubio J., Oteo J. L.

Instituto de Cerámica y Vidrio (C.S.I.C.). Ctra. Antigua Valencia, Km. 24,300.
28500 Arganda del Rey. Madrid. Spain.
Tf: +34 - 91 - 8 71 18 00 Fax: +34 - 91 - 8 70 05 50
* Corresponding author. e-mail:frubio@icv.csic.es

ABSTRACT

In this work we have studied the hydrolysis of titanium tetrabutoxide (TTB) in butyl alcohol. The hydrolysis was carried out by adding H_2O for a molar ratio water/alkoxide of 4. The hydrolysis has been followed by FT-IR spectroscopy, and the evolution of the Ti-O-C bands of the TTB molecule have been analysed. These bands are located at 1130, 1100 and 1039 cm^{-1} and their intensities decrease with the hydrolysis time. However, these bands do not disappear for several days of hydrolysis confirming the difficulty to obtain a completely hydrolysed TTB molecule. Two IR bands have been assigned to Ti-OH groups and adsorbed H_2O molecules. These bands appear at 3660 and 3525 cm^{-1} respectively and they are firstly observed when a white precipitate appears in the solution. This work shows that this study can be rapidly carried out by FT-IR spectroscopy and can also be applied to the well-established sol-gel process.

1.- INTRODUCTION

The sol-gel process of glasses and ceramics has been extensively studied in both scientific and technological fields during the last decades (1,2). Glasses can be obtained through the sol-gel process at low temperatures and with high chemical purity than those obtained through melting the corresponding oxides (3). In a brief description, the sol-gel process consists of the hydrolysis of a metal alkoxide through the addition of H_2O at a given pH and by a careful control of the hydrolysis and polymerization reactions a gelled mass or a precipitate can be obtained. These materials can thus be transformed to their respective oxides by also a careful control of the drying and sintering processes.

Glasses of different chemical composition such as SiO_2, SiO_2-ZrO_2, SiO_2-TiO_2, etc., have been prepared by the sol-gel process (4-6). SiO_2-TiO_2 glasses are of special interest due to their high refractive index and very low thermal expansion (6). These glasses can be obtained by the sol-gel process by hydrolysis and polymerization of their respective metal alkoxides. It is well known that alkoxides of transition metals have different hydrolysis rate and this rate is also very fast compared to that of silicon alkoxide (7). Therefore, if glasses of any SiO_2-TiO_2 composition want to be synthesized and developed then the hydrolysis of both metal alkoxides must be known.

In a previous work (8) we have shown that Fourier Transform Infrared Spectroscopy (FT-IR) can be used for studying the hydrolysis and polycondensation of tetraethylorthosilicate (TEOS). In that study the hydrolysis of the alkoxide group and the formation of linear and polymeric Si-O-Si chains was followed as a function of the reaction time. Here in this work we will study the hydrolysis of TTB, a titanium alkoxide mainly used for preparing glasses and ceramics from the sol-gel process.

2.- EXPERIMENTAL

The hydrolysis of TTB was carried out in alcoholic medium by using H_2O as a hydrolysis agent. We have not used any catalyst (acid or basic) for the hydrolysis reaction. TTB (Aldrich, 90%), n-butanol (BtOH, Aldrich, for synthesis) and deionized-distilled H_2O were used as raw materials. The hydrolysis reaction was carried out at 25 °C and maintaining a vigorous stirring during the whole process. In this study the molar ratio TTB/BtOH/H_2O used was 1/4/4.

Firstly TTB and BtOH were mixed under stirring for 1 hour at the reaction temperature. After that, H_2O was dropwise added for 2 hours. We have given the name of"addition step" to that time (2 hours). A white precipitate was observed when half of the total volume of H_2O had been added, i.e. after the first hour of the "addition step". At this time the molar ratio TTB/H_2O of the solution was 0.5, and therefore it is necessary to add 2 mol of H_2O in order to observe a precipitate in the solution. Finally when the whole H_2O volume was added, the resulting solution and precipitate were maintained for 7 days at the reaction temperature and with constant stirring. We have given the name of"hydrolysis step" to that reaction time (7 days). During the whole process the reaction container was sealed in order to avoid any adsorption of moisture or evaporation.

The hydrolysis of TTB was followed by FT-IR spectroscopy. An FT-IR spectrophotometer (Perkin-Elmer, Mod. 1760 X) with a resolution of 2 cm^{-1} was used in this study. Each spectrum was obtained by adding a drop of the solution between two KRS-5 window crystals by using a microburete. 10 scans were obtained for each experimental spectrum and background was subtracted each time.

3.- RESULTS

The overall reaction between H_2O and TTB consists of hydrolysis and condensation steps, schematically given as:

hydrolysis $$Ti(OR)_4 + 4H_2O \longleftrightarrow Ti(OH)_4 + 4ROH \qquad (1)$$

condensation $$Ti(OH)_4 \longleftrightarrow TiO_2(s) + 2H_2O \qquad (2)$$

however condensation should occur as an oxolation reaction:

oxolation $$Ti\text{-}OH + Ti\text{-}OR \longleftrightarrow Ti\text{-}O\text{-}Ti + ROH \qquad (3)$$

In acidic medium, H^+ ions catalyse the hydrolysis of $Ti(OR)_4$ and also protonate the Ti-OH leaving groups. This protonation inhibits the nucleophilic attack

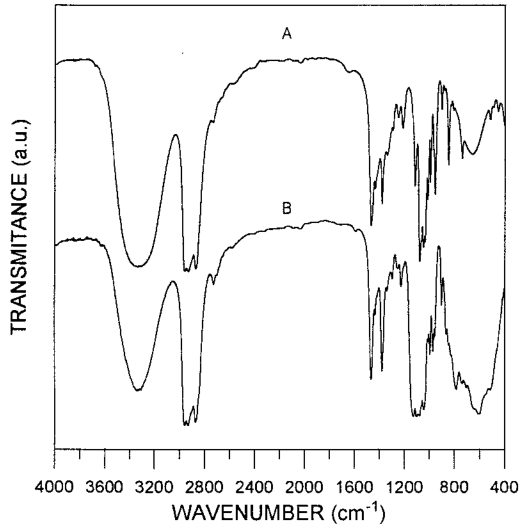

FIG1.- Infrared Spectra of raw materials: A) n-Butanol and B) TTB.

of Ti-OR groups by Ti-OH and then condensation reactions are hindered (9). However, when the hydrolysis is carried out without using any acid catalyst (HCl, SO_4H_2, HNO_3) hydrolysis and condensation reactions proceed simultaneously and precipitation occurs. In accordance with these reactions it is possible to study the hydrolysis of TTB by FT-IR spectroscopy if the solvent (BtOH) gives IR bands which do not overlap with those of TTB. The absence of any acid catalyst allows study of the effect of H_2O in the hydrolysis of TTB.

FT-IR spectra of raw materials, the alkoxide TTB and the solvent BtOH are shown in Figure 1. The spectrum of BtOH gives a broad band about 3330 cm^{-1}, corresponding to the O-H stretching, three bands located at 2960, 2930 and 2868, corresponding to the stretching of C-H bonds in CH_3 and CH_2 groups. Between 1500 and 1300 cm^{-1} the bending vibrations of above mentioned CH_3 and CH_2 groups appear. BtOH shows five medium intensity bands situated at 1114, 1046, 1011, 992 and 953 cm^{-1} and at 1073 cm^{-1} gives a very intense band corresponding to the C-O

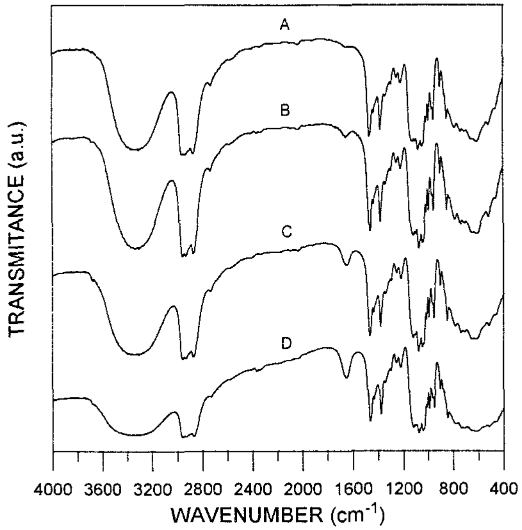

FIG2.- Infrared Spectra of the sol during addition step: A) 0 min., B) 30 min., C) 75 min. and D) 120 min..

bond. Below 900 cm^{-1} different medium and low intensities bands appear. On the other hand, the TTB spectrum also shows a wide band between 4000-3000 cm^{-1} that is also assigned to OH stretching. This band corresponds to the BtOH used as dissolving agent of TTB. The stretching bands of C-H bonds of CH_3 and CH_2 groups of BtOH and TTB are located at 2960, 2930 and 2868 cm^{-1} and between 1500 and 1300 cm^{-1} appear the corresponding bending vibrations. Located at 1070 cm^{-1} the C-O stretching of BtOH is observed. At 1130, 1100 and 1039 cm^{-1} appear the characteristic Ti-O-C stretching vibrations of TTB (10). In the 900-400 spectral region appear different IR bands corresponding to C-H, C-O and Ti-O-C deformation vibrations. In accordance with this results some TTB bands are well defined and not overlapped with those of BtOH, and therefore the hydrolysis of TTB can be followed by the 1130, 1100 and 1039 cm^{-1} bands.

Figures 2 and 3 show the FT-IR spectra of the addition and hydrolysis steps respectively. Spectrum A of Figure 2 corresponds to the starting mixed solution of

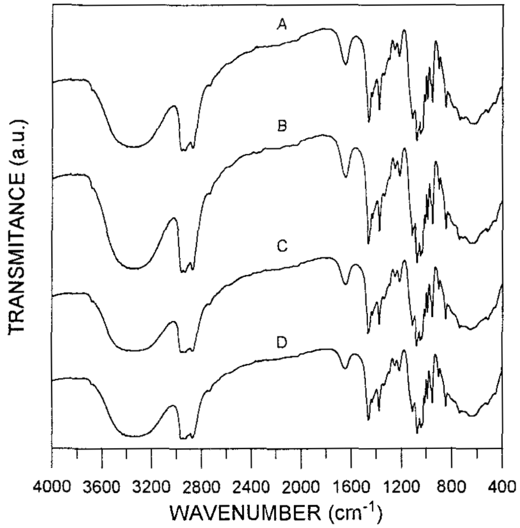

FIG3.- Infrared Spectra of the hydrolysis step: A) 1 day, B) 2 days, C) 3 days and D) 7days.

TTB and BtOH and here the corresponding IR bands of such molecules can also be observed. During the addition step (spectra B-D in Figure 2) different changes also appear in the spectra. Firstly the above mentioned broad band situated at 3330 cm^{-1} increases in both intensity and width. This result corresponds to both the formation of new BtOH molecules due to the hydrolysis of TTB and the presence of non reacted H_2O. The presence of H_2O is confirmed by the 1630 cm^{-1} IR band corresponding to O-H bending vibration of molecular H_2O (8). This band appears during the first moments of the addition step, then increases during the addition step, and decreases continuously up to the end of the hydrolysis step (Figure 3). This result shows that not all H_2O is used for hydrolyzing TTB molecules.

In Figure 2 (spectra B-D) a decrease in the intensity of the Ti-O-C vibration of TTB alkoxide can also be observed. For hydrolysis times lower than 2 hours such Ti-O-C bands can be distinguished from those of BtOH. However for higher hydrolysis times all spectra are very similar to that of BtOH. At the same time, some peaks present in the 800-400 cm^{-1} spectral region decrease in intensity or disappear, and the width of this spectral region also increases. This result corresponds to the formation of Ti-O-Ti bonds according to the condensation reaction given above. The Ti-O-Ti band observed by FT-IR spectroscopy shows wide amplitude and different wide peaks can be observed depending on the crystalline structure (amorphous, anatase, rutile) of the obtained titanium material (11)

Figure 3 shows the spectra corresponding to the hydrolysis step between 1 and 7 days after addition of H_2O. Here all spectra seem unchanged during such hydrolysis time. In order to obtain a more exact interpretation of the above mentioned results we have carried out a deconvolution procedure of the above spectra and after that the area of the different deconvoluted bands have been studied.

4.- DISCUSSION

Spectral deconvolution was carried out assuming gaussian profile of the different IR bands. Firstly, the TTB and BtOH spectra were deconvoluted and the three parameters of each band, intensity, half width and frequency (wavenumber), were determined. These parameters were used as starting point in the deconvolution procedure of the next spectra. After that, each spectrum was deconvoluted by varying mainly the intensities of the IR bands. We have repeated this procedure until we obtain the best fit between experimental and deconvoluted spectra. Calculated deviations were less than 1% in all cases. After that, the area of each deconvoluted IR band was obtained by normal integration. This area is then related to the concentration of the corresponding chemical bond. Figures 4a, 4b, 5a and 5b show different deconvolution curves in the spectral range 4000-2600 and 1175-1000 cm^{-1} respectively, and Figures 6-7 show the evolution of different bands as a function of the hydrolysis time.

Evolution of the IR bands located at 2960 and 1630 cm^{-1} corresponding to the C-H stretching of TTB and BtOH and the O-H bending in molecular H_2O respectively are shown in Figure 6. The C-H band does not change during the whole hydrolysis time and this result shows the absence of vapour losses of TTB or BtOH during the

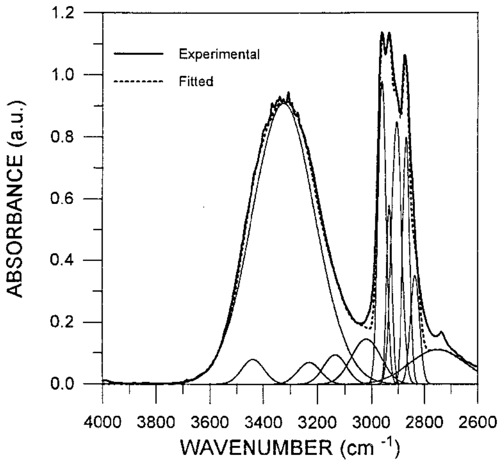

FIG4a.- Deconvolution of the IR spectrum of the sol after 5 minutes of H_2O addition in the spectral range 4000-2600 cm^{-1}.

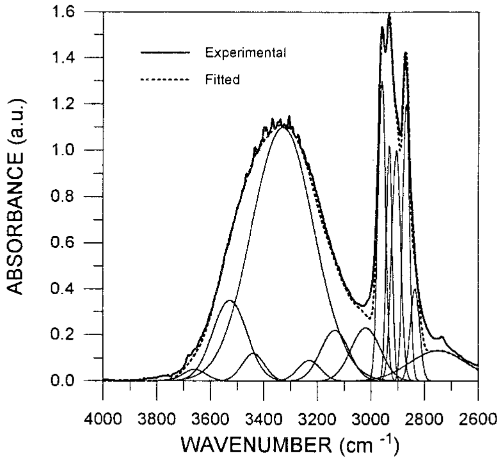

FIG4b.- Deconvolution of the IR spectrum of the sol at the end of the "addition step" (120 minutes) in the spectral range 4000-2600 cm^{-1}.

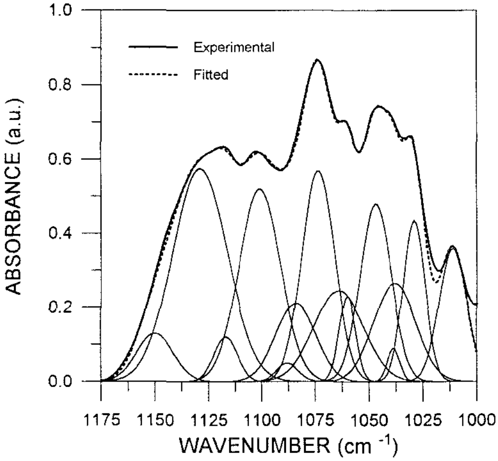

FIG5a.- Deconvolution of the IR spectrum of the sol after 5 minutes of H_2O addition in the spectral range 1175-1000 cm^{-1}.

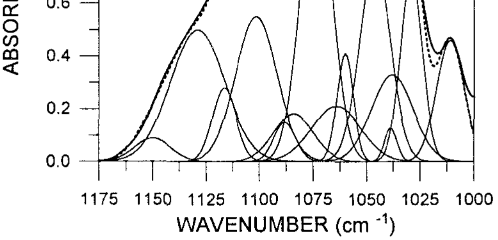

FIG5b.- Deconvolution of the IR spectrum of the sol at the end of the "addition step" (120 minutes) in the spectral range 1175-1000 cm^{-1}.

hydrolysis reaction. During hydrolysis, TTB yields butoxy groups in the form of butanol, but the CH_3 and CH_2 concentrations remain constant as it is observed in this Figure 6. The behaviour of the 1630 cm^{-1} shows that some amount of H_2O used for hydrolysing TTB molecules is not used in the reaction. This result has also been observed by Winter (12) who showed that the hydrolysis of TTB is quantitative up to about 1.5 mol equivalents of H_2O and on further additions only a part enters in the reaction, other part is adsorbed in the precipitate and some part remains in the solvent. According to Figure 6 when H_2O is slowly added to the TTB-BtOH solution an increasing amount of H_2O remains adsorbed on the precipitate and in the solvent.

In order to determine the above conclusion given by Winter we can analyse the deconvoluted spectra shown in Figure 4. Here two new IR bands had to be added (Figure 4-b) in order to obtain the best fit between experimental and deconvoluted spectra, and these new bands are located at 3660 and 3525 cm^{-1}. These high wavenumbers should correspond to OH groups bonded to H_2O molecules through hydrogen bonding (13). Lewis and Parfitt (14) have shown that OH groups on the surface of rutile give three bands at 3740, 3690 and 3660 cm^{-1}, being the first of them due to free Ti-OH groups and the other ones to surface groups which are perturbed probably by hydrogen bonding. Yates (15) showed that perturbed Ti-OH groups of anatase give two bands at 3715 and 3675 cm^{-1}. According to the results obtained for the two crystalline forms of titanium oxide (rutile and anatase) the new bands obtained in this work can be assigned to Ti-OH groups hydrogen bonded to H_2O molecules, where the 3660 cm^{-1} band is due to Ti-OH groups and the 3525 cm^{-1} band is due to H_2O molecules. The evolution of these new bands as a function of the hydrolysis time is also observed in Figure 6. Here the behaviour of such bands is similar to that of the 1636 cm^{-1} assigned to the OH bending of H_2O, showing that they correspond to similar bonds.

The new bands situated at 3660 and 3525 cm^{-1} are firstly observed after the first hour of the "addition step", i.e. when only half of the total volume of H_2O has been added to the reaction solution and, at the same time, when the precipitate was observed as we have mentioned in the Experimental Section. This result shows that

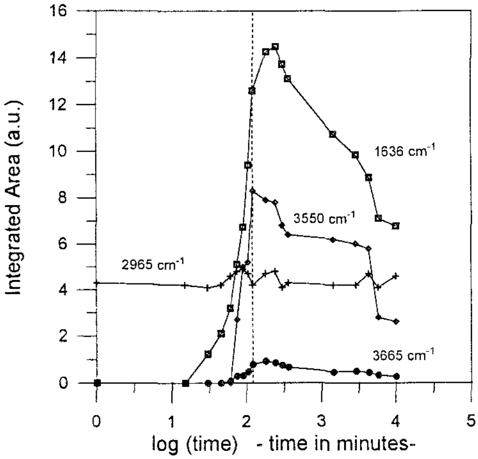

FIG6.- Time evolution of the integrated areas for 3665, 3550, 2965 and 1636 cm^{-1} bands.

these new bands must be associated to the precipitate in accordance with the above discussion.

When the total volume of H_2O used for hydrolysis has been added (two hours), the concentration of H_2O in the solution decreases continuously as it can be observed by the evolution of the 3525 and 1636 cm^{-1} bands indicating that H_2O continues reacting with TTB molecules. At the end of this study, 7 days, some concentration of H_2O remains unreacted in the solution. These H_2O molecules must remain mainly adsorbed on the precipitate as Winter suggested (12).

Figure 7 shows the evolution of the three above mentioned characteristic TTB bands situated at 1130, 1100 and 1039 cm^{-1}. The areas of these bands decrease continuously during the whole hydrolysis study. The high decrease of such band areas correspond to the addition step, and it can also be observed that these bands do not disappear showing that some part of TTB is not hydrolysed. The hydrolysis of titanium alkoxides has been studied in different works (12, 16-18). Different techniques havebeen used in such studies and all of them have concluded that the

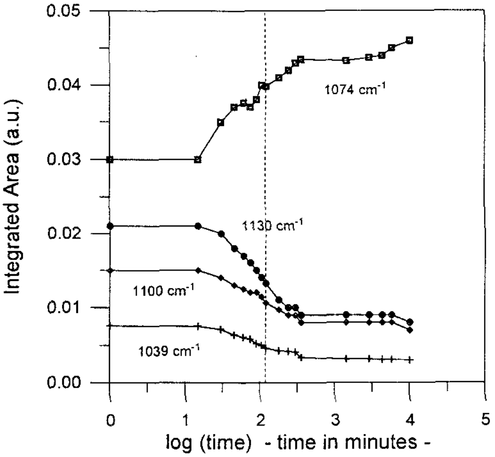

FIG7.- Time evolution of the integrated areas for 1130, 1100, 1074, and 1039 cm^{-1} bands.

fourth alkoxy group of the titanium alkoxide molecule is very difficult to hydrolyse. Bradley et al. (18) studied in an exhaustive form the hydrolysis of titanium ethoxide in ethanol and found that for low molar ratios of H_2O/alkoxide (<1.5) in dilute alkoxide solutions trimeric ethoxide units are cross-linked to form several mixed polymers, but at higher H_2O/alkoxide concentrations the ethoxide behave more as dimers. For H_2O/alkoxide molar ratios higher than 1.7 colloidal precipitates are obtained. Here it was also observed that it was difficult to eliminate the fourth alkoxide group during the formation of mixed polymers and finally colloidal precipitates. Colloidal precipitates obtained for H_2O/alkoxide ratios greater than 1.7 is in accordance with the observation of a white precipitate, as it was explained in the Experimental Section, when 2 mol of H_2O were added to 1 mol of TTB.

Barringer and Bowen (19) have also studied the hydrolysis of titanium tetraethoxide in order to obtain monodisperse TiO_2 particles. They have proposed kinetic equations for hydrolysis and polycondensation reactions of titanium tetraethoxide taking into account that the fourth ethoxide group is hydrolysed during polycondensation of Ti-OH and Ti-OR groups (where R corresponds to ethoxide). Barringer and Bowen used very dilute solutions (0.1-0.2 M) for obtaining monodisperse TiO_2 particles and the molar ratios H_2O/alkoxide used were always higher than 2.5. The high concentration of alkoxide in alcohol that we have used in our work gives a non-disperse precipitate where some alkoxide groups remain unhydrolyzed in spite of the high molar ratio H_2O/TTB used, as it is concluded by the observation of the TTB characteristic bands at the end of the 7 days of reaction. Jean and Ring (20) have shown that for diluted alkoxide solutions (0.075 M) the hydrolysis reactions require more than 1 hour for completion. We show in our work that for concentrated solutions the hydrolysis is not completed after 7 days of reaction.

By assuming that the fourth alkoxide group is removed during the condensation reaction, Barringer and Bowen (19) also gave a general equation in which any titanium alkoxide can be fully hydrolysed by $(2+x)H_2O$ molecules, and a precipitate of general formulae $TiO_2.xH_2O$ is obtained. The value of x proposed was probably between 0.5 and 1.0 in accordance with thermal gravimetric analyses. This result shows that between 2.5 and 3.0 mol of H_2O are necessary for obtaining hydrated TiO_2 particles. Here, our observation of the precipitate in the hydrolysing solution when 2 mol of H_2O have been added to 1 mol of TTB is in accordance with the results of Barringer and Bowen. However, we have also observed that the hydrolysis of TTB is not completed after 7 days of reaction and that adsorbed H_2O remains in the precipitate as was mentioned before by examining the evolution of the 3565 and 1636 cm^{-1} bands. The hydrolysis of the unhydrolyzed alkoxide groups continues during the drying process inside the obtained precipitate, as it is shown in other work (21). The chemical composition of such precipitate must correspond to hydrous titanium oxide with some unhydrolyzed alkoxide groups. The H_2O molecules remaining in the solution and those adsorbed on the precipitate continue the hydrolysis reaction of unhydrolyzed groups but in a low reaction rate in part due to the difficulty to the diffusion of the H_2O molecules through the precipitate.

Figure 7 also shows the evolution of the 1074 cm^{-1} band assigned to C-O bonds of BtOH. The intensity of this band is lower than that of 3300 cm^{-1} assigned to O-H bonds of BtOH, and therefore such bands allow one to follow the formation of butanol during the hydrolysis of TTB (Eq. 1) and by oxolation reaction (Eq. 3). It is observed that the area of this band increases during the whole hydrolysis time (7 days), a result that is in accordance with the decreasing evolution of the TTB bands.

5.- CONCLUSIONS

We have used the FT-IR spectroscopy in order to study the hydrolysis of titanium tetrabutoxide. This study has demonstrated that the FT-IR technique allows us to follow the hydrolysis of titanium alkoxides in a semiquantitative way. The hydrolysis of TTB can be followed by analysing the evolution of the 1130, 1100 and 1039 cm^{-1} bands. These bands decrease during the whole hydrolysis time (7 days) but after that they do not disappear indicating the difficulty of a complete hydrolysis of the TTB molecules. The evolution of the H_2O used in the hydrolysis reaction can also be followed by the IR band situated at 1636 cm^{-1}. The evolution of this band shows that it is necessary to give time for hydrolysis of the TTB molecules by the H_2O ones. At the end of the hydrolysis time some concentration of H_2O remains in the solution in conjunction with unhydrolyzed TTB molecules and adsorbed on the precipitate.

The FT-IR spectroscopy has also given information about the Ti-OH groups formed after the hydrolysis of TTB molecules. They give an IR band situated at 3665 cm^{-1}, and this band is also associated to another band located at 3525 cm^{-1} which has been assigned to adsorbed H_2O molecules. Both bands appear in the FT-IR spectra at the same time as a precipitate is observed in the solution and therefore they are associated to the formation of hydrous titanium oxide particles in which H_2O molecules remain adsorbed on the surface Ti-OH groups.

ACKNOWLEDGEMENTS

We are grateful to CICYT for financial support under project MAT96-0564.

REFERENCES

1. Brinker C. J., Clark D. E., Ulrich D. R. *Better Ceramics Through Chemistry*, New York: Elsevier-North Holland, 1984

2. Klein L. C. Sol-Gel Processing of Silicates. Ann. Rev. Mater. Sci. 1985; 15: 227.

3. Mackenzie J. D. Glasses from Melts and Glasses from Gels. A Comparison. J. Non-Cryst. Solids 1982; 48: 1.

4. Kamiya K., Sakka S. TiO_2-SiO_2 Glasses Prepared from Metal Alkoxides. J. Mater.Sci. 1980; 15: 2937.

5. Gonzalez-Oliver C. J. R., James P. F., Rawson H. Silica and Silica-Titania Glasses Prepared by the Sol-Gel Process. J. Non-Cryst. Solids 1982; 48: 129.

6. Kamiya K., Sakka S. Thermal Expansion of TiO_2-SiO_2 and TiO_2-GeO_2 Glasses. J. Non-Cryst. Solids 1982; 52: 357.

7. Mehrotra R. C. Synthesis and Reaction of Metal Alkoxides. J. Non-Cryst. Solids 1988; 100: 1.

8. Rubio F., Rubio J., Oteo J. L. A FT-IR Study of the Hydrolysis and Polycondensation of Tetraethylortosilicate (TEOS). Spectroscopy Letters. 1998; 31:199.

9. Kallala M., Sanchez C., Cabane B. SAXS Study of Gelation and Precipitation in Titanium-based Systems. J. Non-Cryst. Solids 1992; 147&148: 189.

10. Doeuff S., Henry M., Sanchez S., Livage J. Hydrolysis of Titanium Alkoxides: Modification of the Molecular Precursor by Acetic Acid. J. Non-Cryst. Solids 1987; 89: 296.

11. Vivien D., Livage J., Mazières C. Nature des Précipités D'Oxydes Hydratés des Métaux du Groupe IV A. Part I. Analyse Thermique et Spectroscopie Infrarouge. J. Chim. Phys. 1970;67: 199.

12. Winter G. Esters of Titanium and their use in Paint. Part I: Preparation of Polymeric Butyl Titanates. J. Oil Colour Chem. Assoc. 1953; 36: 689.

13. Farmer V. C. *The Infrared Spectra of Minerals*. London: Mineralogical Society, 1974.

14. Lewis K. E., Parfitt G. D. Infrared Study of the Surface of Rutile. Trans. Faraday Soc. 1966; 62: 204.

15.-Yates D. J. C. Infrared Studies of the Surface Hydroxyl Groups on Titanium Dioxide, and of the Chemisorption of Carbon Monoxide and Carbon Dioxide. J. Physic. Chem. 1961; 65: 746.

16. Boyd T. Preparation and Properties of Esters of Polyorthotitanic Acid. J. Polym. Sci. 1951; 7: 591.

17. Ishino T., Minami S. Hydrolysis of Butyl Titanate. Tech. Rep. Osaka Univ. 1953; 3: 357.

18. Bradley D. C., Gaze R., Wardlaw W. Structural Aspects of the Hydrolysis of Titanium Tetraethoxide. J. Chem. Soc. 1955; 3977.

19. Barringer E. A., Bowen H. K. High-Purity, Monodisperse TiO_2 Powders by Hydrolysis of Titanium Tetraethoxide. 1. Synthesis and Physical Properties. Langmuir, 1985; 1: 414.

20. Jean J. H., Ring T.A. Nucleation and Growth of Monosized TiO_2 Powders from Alcohol Solution. Langmuir 1986; 2: 251.

21. Velasco M . J., Rubio F., Rubio J., Oteo J. L. DSC and FT-IR Analysis of the Drying Process of Titanium Alkoxide Derived Precipitates. Thermochim. Acta. To be Published.

Date Received: August 10, 1998
Date Accepted: December 16, 1998